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(54) Title: SOLAR CONTROL COATINGS AND COATED ARTICLES (57) Abstract A multi-layer coating composites on transparency or glass substrates comprise alternating layers of coatings having high and low refractive index from predominantly inorganic coatings to at least block UV light by a combination of thin film interference and absorption effects. The multilayered coated article has a substrate of clear glass, tinted glass, solar control glass, or colored glass having which is visually transparent to some degree. A first metal-containing predominantly inorganic coating layer that also has some degree of visual transparency and has a refractive index selected from the group of high and low is over the substrate. Over the first coating layer is a second metal-containing predominantly inorganic coating layer that to a degree is visually transparent and has a refractive index opposite from the refractive index of the first coating. Over the second coating layer is a third metal-containing predominantly inorganic coating layer that has a degree of visual transparency and has a refractive index in the range of that of the first coating layer. Additional coating layers can be over, under or interlayered with these first three coating layers to provide different reflective and/or absorption properties.		

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SOLAR CONTROL COATINGS AND COATED ARTICLES

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefits of United States
5 Application Serial No. 60/107,677 filed on November 9, 1998
and entitled "Solar Control Coatings and Coated Articles",
which is herein incorporated by reference.

The present invention is directed to solar control
10 coatings for transparent articles to improve the ultraviolet
reflection and/or near infrared reflection and /or to increase
the visible transmission of the coated article.

Transparent articles such as glass, certain plastics, and
glass and plastic laminates used in such industries as
15 commercial and/or residential construction and remodeling and
motor vehicle and aircraft manufacturing require particular
solar performance properties for these particular industries.
For instance in the automotive industry, designers incorporate
into their designs transparencies as windows and windshields
20 that are both functional and attractive. Heat that builds up
in the passenger compartments of motor vehicles from exposure
to solar energy can be managed with air conditioning systems.
Of course, the larger the build up of heat, the greater the
demand on such systems. Reducing the build up of heat through
25 the windows has become a concern of the designer. Also a
concern with the increasing elaborate nature of the interior
designs within the passenger compartments of motor vehicle is
the effect of ultraviolet ("UV") and IR solar energy on such
interiors. While another factor for consideration is meeting
30 the visible light transmission requirements of government
regulations for particular transparencies like windshields.
So transparencies that provide lower infrared transmittance
and lower total solar energy transmittance are desirable for
reducing the heat gain in the vehicle interior but should also
35 coordinate to some degree with the color of the windshield
transparency. Glass with these properties would be highly
desirable for not only automotive applications but for

architectural use as well. It would further be desirable if the glass was also compatible with flat glass manufacturing methods for ease of production.

For instance in some automotive markets, glass
5 transparencies are needed that have a UV light transmission of less than 10 percent and a total solar energy transmission ("TSET") of less than 50 percent. An attempt at serving this market involves an uncoated substrate that blocks UV light by the addition of titanium dioxide, TiO_2 , and cesium dioxide,
10 CeO_2 in the glass composition. These additives substantially increase the cost of the substrate. This product is only available as a green glass. Organic coatings can be developed with UV and near infrared light ("NIR") absorbing additives to attain the target specifications without the use of CeO_2 .
15 These organic coatings lack the durability usually obtained with uncoated glass substrate.

It is an object of the present invention to have coated transparencies or glass that has reduced ultraviolet light transmission particularly below ten percent for certain
20 automotive markets and to simultaneously reduce the NIR transmission, if possible, with production processes on an economic scale to those of producing solar control glass transparencies.

25 SUMMARY OF THE INVENTION

Multi-layer coating composites on transparency or glass substrates comprise alternating layers of high and low refractive index of predominantly inorganic coatings to at least block UV light by a combination of thin film
30 interference and absorption effects. The amount of UV light transmission is a function of the number of layers and the properties of the substrate. For instance the UV reduction can be obtained with as few as three layers on a solar control glass. This is possible with the alternating layers of
35 titania and silica for rejecting ultraviolet light. In such a case the thickness of the layers is about 300 and about 550 Å, for titania and silica, respectively.

Alternatively or additionally the multi-layered coating composite can have a thickness of about 1041 to 1725 Å, for titania and silica layers, respectively to reject NIR. The TSET of the coated glass can be reduced if the thicknesses of the layers of the multi-layer are appropriately selected. For instance a four layer coating on a green solar control glass can have a TSET less than 37% while simultaneously attaining a low International Standards Organization standard ("ISO") UV target. This type of coating, that reduces both the UV and NIR light transmission, is ideally suited for other substrates that do not have good solar control properties. Also the present invention can involve a four layer multilayered coating composite on the transparency or glass substrate. A four layer titania/silica/titania/silica coating on about a 4.0 mm thick green solar control glass to attain a UV transmission of less than 10%, ISO while maintaining a visible light transmission of greater than 70%. This coating will also reduce the visible light reflection to about 8.0% and a total solar energy transmission ("TSET") < about 45%. Also such a four layered transparency can attain an ISO UV transmission of less than 10% while maintaining a visible light transmission of greater than 70% and reducing the total solar energy transmitted to about 36%. This multilayered coating can also reduce the visible light reflection to <8%. Such a four layer multilayered coating on solar control glass when used as a windshield can be tuned to a windshield installation angle of about 65°. This will reduce the visible light reflection to about 13%.

Another suitable multi-layered coating composite on transparencies or glass substrates can have coatings with additional materials such as fluorine- or antimony-doped tin oxide. With these materials the coatings can impart other properties such as electrical conductivity or solar absorption. Antimony-doped tin oxide, prepared in the appropriate manner, can absorb green light thereby altering the transmitted color of green glass like Sollex® or Solargreen® glass, available from PPG Industries, Inc., from green to

gray. Control of possible changes to the optical properties of coatings with antimony-doped tin oxide because of heat treatment of the coated substrate like tempering or annealing is obtained by the deposition conditions and particular
5 composition of the antimony-doped tin oxide coating.

Additional optional features for the coated transparencies or glass are achieved by the inclusion of additional materials or coatings. For instance, any of the
10 aforescussed multilayered coating composites on substrates can include self cleaning or easy cleaning properties imparted to the coating by depositing the titania in the anatase phase. The self cleaning properties can function even through a surface silica layer. Also the transmitted color of solar control coatings can be modified by substituting a transition
15 metal oxide for all or part of a titania or high refractive index coating layer. In the aforescussed three coating layer composites a fourth coating layer can add an anti-reflection effect and aesthetic options. Also to maintain the reflected color within desired ranges, the thicknesses of
20 these multi-layer coatings can be controlled.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of theoretical light reflectance in percent versus wavelength in nanometers ('nm.") of the light spectrum
25 at curve A for a titania coating with a refractive index of 2.55 on clear glass showing the reflectance over the visible spectrum, where the illuminant was white in an air medium where the substrate is clear glass at a reference wavelength of 380 nm and 0.0 degrees with an ideal detector. Curve B is
30 the reflectance versus wavelength curve for a three layer SHLH coating of titania, H (high refractive index), and silica, L (low refractive index), on float glass.

FIG. 2 shows plots of theoretical reflectance versus
35 wavelength at curve A and curve B for a SHLH coating stack and SHLHLL coating stack, respectively, both on green glass

available as SOLARGREEN® glass. The illuminant, medium detector and angle were the same as for Figure 1.

FIG. 3 shows plots of theoretical reflectance versus wavelength at curve A and curve B for a SLHL coating stack on clear glass substrate with a design wavelength of 330 nm. With and without absorption in the TiO₂ coating layer and no absorption in the SiO₂ coating layer. Other conditions were similar to those for Figure 1.

10

FIG. 4 shows plots of curves A and B of theoretical reflectance versus wavelength for an S3H3L3H3 coating stack and S3H3L3H3LL respectively. The last coating layer for the coating stack for Curve B is SiO₂ at a $\frac{1}{4}$ wave in the visible which is a $\frac{1}{8}$ th wave in the NIR. Other conditions were similar to those for Figure 1 except the design wavelength was 350 nm.

FIG. 5 shows plots of curves A and B of theoretical reflectance versus wavelength for an S3H3L3H3 coating stack as in Fig. 4 for curve A and with fluorine doped tin oxide substituted as part of the middle third of the inner silica coating layer as curve B. The other conditions were the same as those for Fig 4.

25

FIG. 6 shows plots of curves A and B of theoretical reflectance versus wavelength for an S3H3L3H3LL coating stack as in Fig. 4 for curve A and with fluorine doped tin oxide substituted as part of the middle third of the inner silica coating layer as curve B. The other conditions were the same as those for Fig 4.

FIG. 7 shows plots of curves A and B of theoretical reflectance versus wavelength where curve A shows the NIR reflectance peak resulting from the SHLH stack where the TiO₂ is the high index coating layer and the fluorine-doped tin

35

oxide is the low index coating layer. Curve B is for a TCO coating layer added below the SHLH coating stack to have a SMHMH coating stack. The other conditions are the same as those for Figure 1 except the design wavelength is 1000 nm.

5

FIG 8 shows plots of theoretical reflectance versus wavelength of a comparison of a coating stack without a color suppression layer to one with the stack configuration of SM/2HLH. The former is curve A which is curve A of Figure 7 too, and the latter is for curve B. The other conditions are the same as those for Figure 7.

10

FIG. 9 shows plots of theoretical reflectance versus wavelength of a comparison of a coating stack without a color suppression layer, Curve A, which is Curve A of Figure 7 to one with a graded coating layer ("G") as the color suppressant of a coating stack of SGHLH for Curve B. The other conditions are the same as those for Figure 7.

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FIG. 10 shows plots of theoretical reflectance versus wavelength of a comparison of curve A of Figure 7 as curve A to a coating stack of SGLHLH for curve B. The other conditions are the same as those for Figure 7.

20

FIG. 11 shows plots of theoretical reflectance versus wavelength of a comparison of curve A of Figure 7 as curve A to a coating stack of SMHMLH for curve B. The other conditions are the same as those for Figure 7.

25

FIG. 12 shows plots of theoretical reflectance versus wavelength of a comparison of curve A of Figure 7 as curve A to a coating stack of SHLMLMH for curve B. The other conditions are the same as those for Figure 7.

30

FIG. 13 shows plots of theoretical reflectance versus wavelength of a comparison of curve A of Figure 7 as curve A

35

to a coating stack of SHLMH for curve B. The other conditions are the same as those for Figure 7.

FIG. 14 shows plots of solar absorption versus wavelength for several antimony-doped tin oxide coatings indicating that as the amount of antimony increases, the electrical conductivity degrades and the coating starts to significantly absorb solar radiation.

FIG. 15 shows plots of theoretical transmission in percent versus wavelength of a comparison of that for curve A of Figure 7 as curve A to a coating stack of a single coating layer of antimony tin oxide for curve B. The other conditions are the same as those for Figure 7.

FIG. 16 shows the theoretical light transmission curves from a coating stack of G and antimony-doped tin oxide and fluorine-doped tin oxide through a plot of transmission versus wavelength as curve B versus one for curve A of Figure 7 as curve A. The other conditions are the same as those for Figure 15.

FIG. 17 shows the theoretical light transmission curves from a coating stack similar to that of Curve B of Figure 16 but with a thicker antimony-doped tin oxide layer as Curve A and with an outer coating layer of TiO_2 for curve B. The other conditions are the same as those for Figure 15.

FIG. 18 shows the theoretical light transmission curves of that for curve A of Figure 17 and that of curve B for a coating stack with the fluorine-doped tin oxide removed to have a coating stack of graded layer, antimony-doped tin oxide, and TiO_2 . The other conditions are the same as those for Figure 15.

FIG. 19 shows the theoretical light transmission curves of that for curve A which is a single antimony-doped tin oxide

coating on the clear glass substrate similar to curve B of Figure 15 to that for curve B of a coating stack of antimony-doped tin oxide with a reduced thickness to 1800 angstroms with a over coat of titanium dioxide. The latter is a quarter wave optical thickness at 1000 nm. The other conditions are the same as those for Figure 15.

Figure 20 shows the theoretical light transmission for two curves. Curve A is for a five layer coating with a configuration of SHLHLH where H is TiO_2 and L is silica. Curve B is for a coating stack of the same configuration where fluorine doped tin oxide is L. The other conditions are the same as those for Figure 15.

15 DETAILED DESCRIPTION OF THE INVENTION

The transmission of light through a transparent substrate can be modified by the application of inorganic coatings. The inorganic coatings can absorb light and, through thin film physics, can reject light by reflection as well as absorption. Generally thin film means a film thickness of 1 micron or less.

The automotive and architectural markets often require different levels of light transmission depending on the wavelength of light. For instance, it is important in an automobile to have a relatively high transmission of visible light so that the driver can see out of the vehicle, but simultaneously reject the solar radiation that is not in the visible spectrum. The substrate would act as a band pass filter, ideally transmitting all visible light equally, but fully rejecting the UV and NIR parts of the solar spectrum. The occupant would feel more comfortable in a vehicle with this glass and the vehicle would have better fuel efficiency because it could use a smaller air conditioner.

Compromises are usually made between the aesthetics of the glass, the solar performance, and manufacturing constraints. A solar control glass is one that reflects or absorbs rather than transmitting a portion of the light

spectrum, for instance reflecting and/or absorbing some portion of the ultraviolet light spectrum and/or infrared light spectrum and/or visible light spectrum thereby decreasing the transmission of that particular portion of the light spectrum. For instance, tinted products are solar control glasses where the amount of total iron in the finished product generally can be within the range of around 0.5 to around 2 by weight %. Usually at least 20%, preferably in the range 30 to 45% by weight of this total iron content of the finished glass is comprised of ferrous iron. Generally the balance of iron present in the glass as ferrous oxide (FeO) or ferric oxide (Fe₂O₃) has a direct and material effect on the color and transmittance properties of the glass. Also solar control glasses include those which reduce direct solar heat transmittance (DSHT) and/or reduce ultraviolet radiation transmittance while permitting some degree of desirable visible light transmittance. Although it is also possible that such solar control glasses can be privacy glazings. The solar control glasses can reduce problems associated with excessive heating on sunny days while permitting a desirable amount of visible light to pass. Also it is possible that these glasses can maintain a private setting with regards to the interior of the vehicle. The glass used as the substrate of the present invention is one that has some degree of visible transmittance or the glass has at least some degree of transparency so that one can see through the glass to discern an object on the other side. This transparency is less with the privacy glazings of the glass. Three types of solar control glass have gained in popularity, due as much for solar performance as from aesthetic concerns. They are SOLARGREEN® glass and SOLEXTRA® glass, which are green and blue, respectively. The SOLARGREEN glass substrate is a, solar control glass available from PPG Industries, Inc. having an LTA level of 71%, a TSET of 42.9%, and a performance ratio of 1.65. The dominant wavelength of this glass substrate is 512 nm and its color as described in the CIELAB color system is L* = 88.3, a* = - 8.7, b* = 3.5 and C* = 9.4. In addition, the

hue angle of the substrate is 158°. It should be appreciated that although the color of the particular substrate is characterized as "green," this glass includes a slight yellowish coloration as is apparent from its a*, b* coordinates. Manufacturing constraints and federal regulations on visible light transmission have hindered the commercialization of solar control glass (TSET=50%) with other aesthetics. Generally a solar control glass has a Total Solar Energy Transmission of less than 50 percent (TSET <50%).

10 Examples of such glasses are those commercially available or Solargreen® glass Solextra® glass and those described in U.S. Patents 5,830,812; 5,023,210; and 4,873,206 all hereby incorporated by reference.

Solargreen® and Solextra® glass have focused on minimizing total solar energy transmitted (TSET), rather than targeting a specific part of the spectrum such as UV light. Recently, the automotive market in Japan has started to shift toward a glazing requirement that has a UV light transmission less than 10% while maintaining the TSET level comparable to Solargreen® glass. A commercial version of this glass is known as Solarblock® glass available from PPG Industries Inc. The low UV light transmission is due to high levels of an expensive additive, CeO₂. The application of a coating in accordance with the present invention can attain the UV transmission target and has the possibility of adding features while simultaneously giving a cost advantage compared to the uncoated substrate, which can be essentially free of CeO₂.

The various thin film coatings with a degree of transparency of the present invention will reduce the transmission of UV light while optionally imparting additional properties such as anti-reflection, lower TSET, and/or self cleaning attributes and different reflected or transmitted colors. The combination of the various coatings provides several properties together in one coated glass product which can give a cost as well as a performance advantage. The thin film structures described below have one to five layers made up of several preferably one to four materials. The materials

are selected for different characteristics. In order to capitalize on the physics of thin films, materials with different refractive indices (RI) are used. In addition, the materials should be physically and chemically durable and, if possible, contribute other properties such as absorption of light in different parts of the solar spectrum.

For refractive index generally a high refractive index is merely one that is higher than a low refractive index and vice versa for a low refractive index. Preferably a high refractive index is greater than 1.9 and a low refractive index is less than 1.6 and a medium refractive index is between 1.6 and 1.9. Although the dividing lines for these ranges is not a stark line and the RI at the extremes of adjoining ranges may cross over between the adjacent regions to a degree.

Non-exclusive examples of suitable materials for the high and low refractive index coatings layers include various metal oxides, nitrides, and their alloys and mixtures. For the higher refractive index materials include: zinc oxide (refractive index = 1.90), titanium oxide (TiO₂) (refractive index = 2.3-2.7), CeO₂ (refractive index = 1.95), antimony oxide (Sb₂O₅) (refractive index = 1.71), SnO₂, ITO (refractive index = 1.95), Y₂O₃ (refractive index = 1.87), La₂O₃ (refractive index = 1.95), zirconium oxide (ZrO₂) (refractive index = 2.05) and tin oxide, and indium oxide. Also alloys and mixtures of these can be used. The doped oxides have a very low refractive index in the near infrared region due to the free electrons in the material. The fluorine and/or indium doped tin oxides has a higher refractive index than that of antimony doped tin oxide. Nonexclusive examples of the materials for the low index coating layers may include silicon dioxide, SiO₂ (about 1.45), Al₂O₃ (about 1.65), B₂O₃ (about 1.60), silicone polymer, magnesium oxide, and cryolite.

The preferred coatings discussed below are made up of four different coatings. The first layer can be titania or TiO₂. This material has a very high refractive index, absorbs UV light, is chemically inert and durable and, when deposited

in the anatase form, is photocatalytic. The second material is silica or SiO_2 . This material is also chemically inert and durable and it has a very low refractive index.

Most of the structures described below could be made with just these two materials, but two additional materials can be used for their unique properties. The first is fluorine-doped tin oxide. This material is electrically conductive and has a high refractive index in the UV and visible part of the spectrum and a low refractive index in the NIR part of the spectrum. This property allows unique features to be designed into various coatings. The fourth material is antimony-doped tin oxide. This material absorbs light across the entire solar spectrum and more importantly, control of the relative absorption at different wavelengths is achieved by altering the deposition process. It is possible to tune the coating to absorb relatively more visible light or UV light or NIR light. A very unique property of this material is that it can have a very high absorption of green light. By placing this coating on a green glass we can change it to a gray glass, thus creating a high performance solar control glass with neutral aesthetics.

By dealing entirely with durable oxide coatings, these structures should be suitable for tempered automotive parts.

Other materials can be used with this basic set and they will be considered as needed. But these four materials can be used to make many different coatings with substantially different optical properties. One on-line float glass process, as well known to those skilled in the art, could be used to make all of these products simply by selecting which materials to deposit, in what order and at what thicknesses.

All of these basic coatings can generally be applied in a manner similar to the electroconductive coatings on windshields as described in U.S. Patent 4,610,771 hereby incorporated by reference. This on-line effort can utilize similar equipment to produce these novel coatings on a solar control glass substrate. Any other known method in the art for deposition of any of these coating layers can be utilized,

for instance by sputtering under vacuum at a radio-frequency can be employed. Also other techniques can be used such as cathodic sputtering, particularly by CVD plasma from an appropriate siliceous precursor or by a gas phase pyrolysis
5 under ambient pressure.

The sections that follow detail specific coating constructions, results of optical models, and sensitivity analysis. Although not limiting to the present invention, the theory behind the various structures is introduced as more
10 functionality is built into the coatings.

The UV blocking coating is the simplest of the solar control coatings discussed herein, and the physics behind it is common to many of the other designs.

15 The interaction of light with any substrate, coated or not, must conform to the following formula.

$$A + R + T = 100\%$$

Equation 1

20 The percentage of light absorbed (A) plus the percentage of light reflected (R) plus the percentage of light transmitted (T) must add up to 100 percent. If more light is reflected by a coating then less will be absorbed and/or transmitted. The function of the UV reflection coating is to
25 reflect as much UV light as needed to meet a transmission target of less than 10% for the coated glass article. Some UV light will be absorbed by the coating and glass substrate, but most of the transmission loss is due to a high reflection attained through appropriate selection of layer materials and
30 thicknesses. More or less layers may be needed depending on the UV absorption properties of the substrate. Specific examples will be discussed below.

The maximum reflection attained by a single high index layer on a substrate is easily calculated and this type of
35 layer is known as a quarter wave layer. The thickness of the quarter wave layer is calculated with the following formula:

$$h = \lambda / (4 \text{ multiplied by } n_1), \quad \text{Equation 2}$$

where h is the thickness of the layer, λ is the wavelength that maximum reflection occurs (design wavelength) and n_1 is the refractive index of the coating at the design wavelength.

If the refractive index from the material or materials of the coating is large or high then the layer is designated with an "H" and if the refractive index is low it is designated with a "L" and medium or in-between an "M". A coating stack can be easily abbreviated with this terminology. For instance, an anti-reflection coating with a quarter wave of a medium index material next to the glass and a half wave (two quarter waves) of a high index material next and a quarter wave of a low index material on top would be designated as SMHHL, where S indicates the substrate. It should be noted that each layer is a quarter wave only at the wavelength for maximum reflectivity in the desired portion of the light spectrum.

The intensity of the reflection is calculated using equation 3.

$$R = [(n_1^2 - n_0 n_s) / (n_0 n_s + n_1^2)]^2, \quad \text{Equation 3}$$

where R is the reflectance, n_s is the refractive index of the substrate and n_0 is the refractive index of the incident medium and n_1 is the refractive index of the coating. The incident medium in the environment in which the substrate exists, i.e., air or otherwise for laminate structures. For a titania coating with a refractive index of 2.55 at a wavelength of 380 nanometer (nm) on a clear substrate with a refractive index of 1.51, the quarter wave thickness of the titania layer would be 372Å and the reflectance would be 26.5%. This reflectance is from the coated surface only. Absorption in the coating is neglected for the next several examples but absorption will be noted when included.

The reflectance over the visible spectrum is shown in Figure 1 at Curve A. One can see from Curve A of Figure 1 that the maximum reflectance occurs at the design wavelength, 380 nm, and that the reflectance is decreased at all other wavelengths across the solar spectrum.

The reflectance from the first surface of a substrate at normal incidence is given by the following equation:

$$R = [(n_0 - n_s) / (n_0 + n_s)]^2, \quad \text{Equation 4}$$

where n_0 and n_s are the refractive indices of the incident medium and the substrate, respectively. The application of a quarter wave layer to a substrate creates a coated substrate with an equivalent refractive index, n_{1e} , given by the formula:

$$n_{1e} = n_1^2 / n_s \quad \text{Equation 5}$$

The new equivalent refractive index can then be substituted for the substrate refractive index in equation 4 to calculate the new reflectance for the coated substrate. This new equation is listed here:

$$R = [(n_0 - n_{1e}) / (n_0 + n_{1e})]^2, \quad \text{Equation 6}$$

Equation 6 is equivalent to equation 4 above.

The equivalent refractive index for a substrate and coating stack designated as SH(LH)^m can be calculated using the following formula:

$$n_e = (n_H^2)^{m+1} / (n_L^2)^m n_s \quad \text{Equation 7}$$

The reflectance of an arbitrary number of layers can then be calculated using equations 6 and 7, wherein "m" is the number of HL or LH pairs in the coating stack.

A three layer SHLH coating of titania, H, and silica, L, on float glass would have an equivalent refractive index of:

$$n_e = (2.6^2)^{m+1} / (1.45^2)^m 1.51 = 14.4 \text{ and a reflectance of}$$

$$R = [(1 - 14.4) / (1 + 14.4)]^2 = 75.6\%.$$

The reflectance versus wavelength curve for this coating is shown in the following Figure 1 at curve B.

Table 1 summarizes the performance for some illustrative examples and predictive examples of a one, three and five layer coating on clear, and solar control glasses of SOLEX[®] and SOLARGREEN[®] glass.

Table 1

Example	Substrate	Coating with Stack Substrate	Visible Reflectance	Visible Transmission	ISO UV Transmission	Total Solar Energy Transmitted
Illustrative example A	Clear ¹	SH	28.99	69.14	43.41	69.66
Example 1	Clear ¹	SHLH	27.51	70.51	20.24	69.49
Example 2	Clear ¹	SHLHLH	15.59	82.2	8.39	68.71
Illustrative example B	Clear ¹	None	7.9	89.71	64.59	82.74
Illustrative example C	Solex Glass ¹	SH	28.47	62.08	20.14	45.53
Example 3	Solex Glass ¹	SHLH	27.11	62.94	9.03	44.86
Example 4	Solex [®] Glass ¹	SHLHLH	15.04	73.78	3.47	44.3
Illustrative example D	Solex [®] Glass ¹	None	7.37	80.5	30.73	55.32
Illustrative example E	Solargreen [®] glass ²	SH	28.16	56.33	12.17	35.44
Example 5	Solargreen [®] glass ²	SHLH	26.78	57.08	5.42	34.83
Example 6	Solargreen [®] glass ²	SHLHLH	14.6	67.11	2.06	34.52
Illustrative example F	Solargreen [®] glass ²	None	6.84	73.16	19.37	43.54

S = Substrate

H = TiO₂, 1/4 Wavelength at 380 nm

L = SiO₂, 1/4 Wavelength at 380 nm

¹ substrate thickness is 4 mm

² substrate thickness is 3.6 mm

10 The optical constants for the silica and other materials versus wavelength were developed in the art recognized manner considering the constituents of the coating composition, and manner of disposition, and thickness of the coating. The reflectance curves of the figures were generated using TFCalc,

a commercial software applications for thin film calculations available from Software Spectra Inc.

UV REFLECTION WITH ANTI-REFLECTION

5 A feature of the simple SHLH configuration described above is the relatively high visible reflectance. The high reflectance can limit the utility of this approach when applied to solar control glasses with uncoated visible transmission near the 65 to 70 percent range. The high
10 reflectance will reduce the visible transmission below the 70% limit, for instance, when applied to SOLARGREEN® glass for a windshield application.

 This limitation can be alleviated by the application of a half wave layer on top of the SHLH stack. A half wave layer
15 at the design wavelength is an absentee layer since it is optically invisible at the design wavelength. Therefore, at the design wavelength the substrate and coating stack of SHLHLL behaves the same as the stack SHLH and there is no alteration of the UV rejection performance. For our case with
20 a design wavelength in the UV, the top half wave of silica LL, is a quarterwave in the visible spectrum. This layer then acts a visible spectrum reflectance reducing layer. The design wavelength and/or layer thicknesses can then be optimized for the desired UV reflectance and visible light
25 transmission requirements. The SHLH and SHLHLL coatings are shown in Figure 2. These coatings have a design wavelength of 330 nm. This design wavelength minimizes ISO UV while for 3.6 mm Solargreen® glass maintains a visible light transmission well above 70%. Curve B is the stack SHLHLL and curve A is
30 the stack SHLH.

 Additional pairs of LH can be added between the top H layer and the LL layer to further reduce the UV light rejection properties of the coating stack. The visible reflectivity of this stack on Solargreen® glass for various
35 design wavelengths is shown in Table 2. As can be appreciated from this table, selection of the appropriate design wavelength can have an appreciable effect on the properties of

the resultant coating. As noted above these predicative examples were generated with the TFCalc software.

Table 2

Substrate	Substrate Thickness	Coating Stack	Design Wavelength	Visible Reflectance	Visible Transmission	ISO UV Transmission
Solargreen	3.6 mm	SHLHLL	220 nm	4.04	75.41	18.54
Solargreen	3.6 mm	SHLHLL	230 nm	3.79	75.58	18.35
Solargreen	3.6 mm	SHLHLL	240 nm	3.86	75.5	17.95
Solargreen	3.6 mm	SHLHLL	250 nm	4.2	75.21	17.26
Solargreen	3.6 mm	SHLHLL	260 nm	4.73	74.78	16.23
Solargreen	3.6 mm	SHLHLL	270 nm	5.37	74.26	14.93
Solargreen	3.6 mm	SHLHLL	280 nm	6.06	73.71	13.51
Solargreen	3.6 mm	SHLHLL	290 nm	6.72	73.19	12.12
Solargreen	3.6 mm	SHLHLL	300 nm	7.31	72.73	10.87
Solargreen	3.6 mm	SHLHLL	310 nm	7.82	72.33	9.81
Solargreen	3.6 mm	SHLHLL	320 nm	8.26	72	8.96
Solargreen	3.6 mm	SHLHLL	330 nm	8.67	71.7	8.33
Solargreen	3.6 mm	SHLHLL	340 nm	9.12	71.35	7.87
Solargreen	3.6 mm	SHLHLL	350 nm	9.71	70.88	7.58
Solargreen	3.6 mm	SHLHLL	360 nm	10.55	70.21	7.43
Solargreen	3.6 mm	SHLHLL	370 nm	11.73	69.25	7.42
Solargreen	3.6 mm	SHLHLL	380 nm	13.35	67.93	7.54
Solargreen	3.6 mm	No Coating		6.84	73.16	19.37

5

In Table 2 the last Examples is illustrative and the others are predictive.

It can be seen from Figure 2, that the reflectance of both coatings remains the same at the design wavelength (330nm) and the reflectance curve is substantially modified throughout the rest of the spectrum. The halfwave of silica, since it acts as an anti-reflective ("AR") layer, maintains, or increases, the visible light transmission, thereby improving the utility of this UV rejection coating for more substrates. If the transmission of light through the coated substrate is increased, then the substrate could be modified to absorb more solar radiation while simultaneously maintaining its visible light transmission requirements. The glass composition of the solar control glass can be modified to reduce the TSET to about 40% and the visible transmission increases from an average performing AR coating.

20

The examples listed above were made using optical constants for coatings without absorption coefficients to easily demonstrate the effects of interference coatings on the optical properties of glasses. But in reality, coatings absorb some light and therefore have non-zero absorption coefficients. Several of the above examples will be repeated using coatings that have different optical constants to demonstrate the effect of absorption on the transmission spectrum of the coatings. In practice, one would select the appropriate materials and design construction to best meet all of the desired attributes needed for the coated glass.

Figure 3 shows the transmission curves for a SLHL stack with and without absorption in the TiO₂ layer. There is no absorption in the SiO₂ layer. Curve B is without absorption and curve A is with absorption.

UV and NIR BLOCKING

The addition of solar control or decreasing the TSET of the coated substrate can be attained by other means than those described above. This section describes several routes to lowering the TSET while simultaneously lowering the UV transmission of the coated substrate.

A. HLH

The previous examples of Table 2 showed how a half wavelayer can be added without changing the performance at the design wavelength. Therefore, an initial SHLH stack designed for 350nm and with halfwave layers to each layer gives the stack, S3H3L3H (HHHLLLHHH). This coating behaves identically at the 350nm design wavelength, but now becomes a SHLH stack at near 1050nm. The reflectance maximum does not exactly occur at 1050nm because the refractive index of the coatings is less at the longer wavelengths. The peak is therefore, shifted to shorter wavelengths in the near IR ("NIR") part of the spectrum. In this manner, we now have a coating that reflects at two design wavelengths. The example uses the TiO₂ considering absorption and SiO₂ without considering absorption

and the coating is on 4.0 mm clear glass. The curve is shown in Figure 4 as curve A.

B. HLHL/2

5 The intensity of the reflection in the visible spectrum can be altered by the application of a $1/4$ wave in the visible spectrum. This layer would be a $1/8$ wave in the NIR at 1050nm and a 1.5 wave in the UV at 350nm. The intensity of the reflection in the NIR will be reduced slightly as a
10 tradeoff to lower visible reflectance and high visible transmittance. The curve for this coating is shown in Figure 4 as curve B. The reflectance, for the coating on clear glass, drops from about 17 to about 6%. Curve B has the SiO₂ top layer and curve A does not.

15

C. Addition Properties

 The previous two embodiments were directed to a three layer coating that reflected light in both the UV and NIR parts of the spectrum. Earlier it was indicated that the
20 intensity of the reflected light is a function of the number of alternating high and low refractive index layers. More layers means higher reflectance. But as more layers are added to a dual reflectance coating the overall thickness becomes a problem. The cost increases and more coaters are needed to
25 produce the coating in a float line environment.

 The intensity of the UV reflectance can be increased without increasing the total thickness of the stack or sacrificing the intensity of the NIR reflectance. This is accomplished by substituting part of the middle third of the
30 inner silica layer with fluorine-doped tin oxide. Put another way the middle layer becomes a combination of several layers. The fluorine-doped SnO₂, like most transparent conducting oxides, has the unique property of having a high refractive index in the UV and visible spectrum but has a low refractive
35 index in the NIR. The coating then in the UV is S3HLHL3H and in the NIR is SHLH. The coating is effectively a five layer coating in the UV and visible but reduces to a three layer coating in the NIR. The reflectance for this coating and the

S3H3L3H are shown in Figure 5 and this coating with a visible quarter wave silica layer and the S3H3L3HLL are shown in Figure 6. The "B" curves for these figures are the designs with the addition of the fluorine doped tin oxide layer and the "A" curves are without.

TRANSPARENT CONDUCTING OXIDES ("TCO")

Transparent conducting oxides can be used in HLH stacks to increase the reflectivity of light in the near IR with a high refractive index material as shown above because they have a low refractive index in the NIR region believed to result from the free electrons and their mobility in the crystal lattice. They therefore have utility beyond the example cited above for a combination UV/NIR blocking design. Curve A of Figure 7 shows the NIR reflectance peak resulting from a SHLH stack where TiO₂ is the high index layer and fluorine-doped tin oxide is the low index layer.

As can be seen in this Figure 7 at Curve A, the coating stack will reflect about 58% at the design wavelength of 1 micron. The refractive indices in the visible region are different also and this results in interference peaks and reflected color. This trait is considered objectionable and a means to maintain the reflectance peak while minimizing the reflected can be attained by either of two methods i.e., coatings above or below the stack. The key is to add layers that will alter the visible light reflection properties without significantly attenuating the NIR peak. One way to do this is to add a coating that is optically active in the visible region and optically inactive in the NIR region. A conductive transparent oxide ("TCD") is good for this purpose. As mentioned above the refractive index of a TCO is low in the NIR and moderate in the visible spectrum, relative to TiO₂. When added below the SHLH stack above we get a stack of the configuration, substrate, moderate index, high index, moderate index and high index in the visible and SL/3HLH in the NIR spectrum. The designation SMHMH for this coating is not used because the layers are not quarter wave optical thickness in the visible region. The L/3 layer is optically inactive as

shown in Figure 7 at curve B where the plot of this stack is compared to the stack of curve A. Curve A is the normal line and curve B is the bold line for the L/3 containing stack. One can see that the NIR peak is relatively unchanged while the visible peaks are damped substantially. This stack would have a TSET of about 57% and a visible transmission of about 76%. This coating would also have a low emissivity due to long wavelength reflection of light by the transparent conducting oxide. The reflectance peak can be increased as mentioned previously by additional LH pairs of layers.

Another means to dampen the reflected color is by adding a coating of intermediate refractive index in both the visible and NIR spectrum. One might expect that the NIR reflection would be attenuated by a layer of intermediate refractive index between the substrate and the first high index layer since it would disrupt the proper sequence of HLH needed for reflection enhancement. Surprisingly, the intensity of the reflectance peak is not attenuated, but the peak is simply shifted slightly in wavelength. The peak can be moved back by adjusting the other layers in the stack. This result allows for adjustment of the color of the stack without sacrificing NIR reflection performance. Figure 8 compares a coating stack without a color suppression layer as Curve A, which is Curve A of Figure 7 also, to one with the stack configuration SM/2HLH. One can see that the visible reflectance peaks are dampened while the NIR peak is subtly shifted.

Still another way to dampen the color is to add a graded index layer beneath the coating stack. This layer generally has an increasing (or decreasing) refractive index with increasing film thickness through the film layer. This type of color suppression is well known for suppressing the color of a single coating (see U.S. Patents 5,356,718; 5,599,387, hereby incorporated by reference). This type of color suppression has not been examined for use in suppressing the color of a stack of coatings and more importantly, its effect on the NIR reflection from such a stack has been unexamined. The graded index coating can both suppress color and in some

cases improve performance in a HLH stack. The gradient layer used in these examples is modeled as a ten layer coating, which I will designate with a G, with each layer being 10nm thick and whose indices vary from 1.55 the glass interface to 2.0 at the top of the graded layer. The reflectance curve, again compared to the SHLH stack of curve A of Figure 7, is shown in Figure 9. Our stack is now SGHLH. For curve B with the graded layer the peak reflectance is only slightly reduced and shifted in wavelength and the visible reflectance is substantially dampened.

The reflectance peak can now be further increased because the gradient layer creates a higher interface than that of the glass and the addition of another fluorine-doped tin oxide layer median the graded index layer and the first high index layer will now be optically active and will result in a increase in the reflectance peak. The stack is SGLHLH. The color is still dampened but the performance is increased. This stack would be very good when lower emissivity is needed. The reflectance spectrum, compared to curve A from Figure 7, is shown below in Figure 10.

The fluorine-doped tin oxide coatings also absorb some NIR light and are therefore, ideally suited for solar control applications. They contribute to reductions in NIR light transmission through both reflection and absorption.

Also, unexpectedly, a pair of high/low index layers much less than a quarter wave optical thickness can be used to dampen the reflected color. They also do not effect the NIR reflection substantially.

Adding a layer above the stack will result in a reduction of reflection as described above and this method is suitable here also. By adding a layer above and below the coating stack we can effect both reflected color and intensity reduction. The stack would have a moderate refractive index, high, moderate, high and then low (MHMHL). The resultant coating stack, compared to curve A from Figure 7 is shown in Figure 11. The visible intensity is substantially dampened and the color is neutral. There is some shift in the

intensity of the reflectance peak, but this can be corrected for by adjusting the thicknesses of the HLH layers.

Combinations of SiO₂ and a TCO can be used in combination for the low index layer as described above for the dual NIR/UV rejection coating. A stack having the substrate, TiO₂, SiO₂, Fluorine-doped tin oxide, SiO₂, Fluorine-doped tin oxide, and TiO₂ with the SiO₂ and Fluorine-doped tin oxide (SHMLMH) having a combined optical thickness in the NIR of a quarter wavelength is shown in Figure 12 along with the curve A from Figure 7 for comparison. As can be seen from Figure 12, the reflectance peak is enhanced with this multi-layer low index quarter wave approach. Also note that the visible reflectance peaks are attenuated somewhat.

The new ability to attenuate the visible reflectance spectrum with this multi-layer approach for a low index layer can be used regarding the visible reflectance spectrum for reduced reflected color while maintaining the NIR reflectance peak. As an example, a stack having a substrate, TiO₂, SiO₂, SnO₂:F and TiO₂ (SHLMH) will have no reflected color and an enhanced reflection peak as shown in Figure 13. Again the reflectance curve A from Figure 7 is included for comparison. The inclusion of layers that are optically active in the visible and combine to be of low index in the NIR spectrum can be used to attain any desired visible optical effect desired by the designer and is not limited simply to color suppression.

The addition of antimony to tin oxide in doping levels will impart electrical conductivity. As the amount of antimony increases, the electrical conductivity degrades and the coating starts to significantly absorb solar radiation. Figure 14 shows the solar absorption of several antimony-doped tin oxide coatings. The chemical vapor deposition ("CVD") process parameters that produced these coatings are listed in Table 3. Of course other known deposition processes can be used such as pyrolytic coating techniques and sputter coating techniques like MSVD magnetron sputtered vacuum deposition. The spray coating was made as a 5 weight percent mixture.

Table 3 (SLM is Standard Liters/min)

SAMPLE #	GLASS TEMP. DEG. F	MBTC CONC. MOLE %	WATER CONC. MOLE %	GAS FLOW SLM	EXHAUST RATIO % OF GAS	GLASS THICK. MM	LINE SPEED "/MIN
1	1000	0.5	0.5	55	115	4	50
2	1200	0.5	0.5	55	115	4	50
4	1200	0.5	0.0	55	115	4	50
6	1200	0.1	0.5	55	115	4	50
8	1200	0.1	0.0	55	115	4	50
9	1000	0.5	1.0	55	115	4	50
10	1000	1.0	0.5	55	115	4	50
11	1000	1.0	1.0	55	115	4	50

The mixture was of antimony trichloride in monobutyl-tin trichloride (MBTC) and the mixture was hand sprayed onto a clear glass substrate heated to about 1150 degrees F. The antimony was fed into the CVD experiments 1 to 11 at a constant 20 weight % relative to the MBTC. The coater had a central inlet slot with upstream and downstream exhaust slots. The width of the coating zone was four inches and the contact length between exhausts was five inches. Air was used as the carrier gas.

In Table 3, coatings 4 and 8 absorb more NIR light than visible light, making the coatings good for solar control when high visible light transmission is needed. Coatings 2 and 6 have peak absorption at about 550nm. These coatings are well suited for muting the green color of Sollex[®] glass and Solargreen[®] glass. Coating 10 absorbs more visible light than NIR light, coating 1 absorbs a relatively constant amount across the solar spectrum and coatings 9 and 11 absorb appreciable UV light.

A significant issue for coatings that will be glazed in the annealed and tempered states is color fastness, or color that does not change when the coated glass is heated. The appearance and performance is preferably the same before and after heat treating. The antimony doped tin oxide coatings studied for this project may or may not change upon heating, depending on deposition parameters. The properties of various samples and how certain properties change with heat treating are listed in table 4. The sample numbers with an H after them indicate the samples after heat treating.

Table 4 (Part A)

Average Film		Hall Mobility MMR H-50 (cm ² /Vs)	Hall Carrier Conc. MMR H-50 (¹ E20 Carr./cm ³) ¹	Hall Surf. Resist. MMR H-50 (ohm/sq.)	Unweighted Absorption	
					UV-Vis 300-700 nm	UV-Vis 300-2500 nm
Sample	Thickness	Avg.	Avg.	Avg.		
1	665	7.52	2.35	3.E+05	0.159	0.191
2	795	0.72	1.49	7.E+03	0.307	0.298
4	310	0.54	4.57	9.E+03	0.173	0.256
8	153	0.54	4.95	2.E+04	0.142	0.211
10	675	6.70	6.03	2.E+06	0.203	0.214
11	879	4.90	9.48	6.E+05	0.254	0.224
1H		1.02	1.07	3.E+05		
2H		0.47	2.23	8.E+03		
4H		0.42	4.89	1.E+04		
8H		0.35	4.84	2.E+04		
10H		0.04	3.41	2.E+05		
11H		8.35	1.92	2.E+05		

5 ¹ Exponent (E) multiplied by 10²⁰ electron carrier /cm³

Table 4 (Part B)

Sample	T	Tx	Ty	R1Y	R1X	R1Y	R2Y	R2X	R2Y
1	67.7	0.312	0.312	21.0	0.299	0.307	17.6	0.294	0.303
2	50.2	0.295	0.298	21.8	0.333	0.337	16.3	0.324	0.327
4	76.5	0.306	0.316	12.2	0.294	0.297	09.2	0.280	0.284
8	85.0	0.307	0.317	09.2	0.301	0.308	08.0	0.295	0.302
10	76.0	0.313	0.321	16.0	0.294	0.302	13.4	0.295	0.305
11	67.9	0.309	0.316	21.3	0.318	0.330	17.6	0.318	0.333
1H	70.1	0.312	0.320	19.2	0.298	0.306	16.6	0.293	0.303
2H	52.5	0.296	0.301	21.5	0.326	0.330	16.0	0.315	0.318
4H	76.7	0.306	0.316	12.2	0.294	0.297	09.2	0.280	0.284
8H	85.1	0.307	0.317	09.2	0.301	0.308	08.0	0.295	0.302
10H	72.1	0.312	0.320	18.3	0.295	0.304	16.1	0.291	0.302
11H	69.3	0.309	0.317	20.5	0.313	0.325	18.1	0.309	0.326

5

Table 4 (Part C)

Sample	Delta T	Delta R1	Delta R2	Macadam T	Macadam R1	Macadam R2
1	2.38	-1.78	-0.96	3.21	4.98	3.32
2	2.25	-0.32	-0.30	3.79	5.16	6.56
4	0.14	-0.02	0.01	0.26	0.10	0.19
8	0.12	-0.07	-0.02	0.18	0.31	0.15
10	-3.9	2.32	2.68	4.74	7.38	9.96
11	1.34	-0.81	0.49	1.90	4.48	6.94

R1 is the reflectance from the coated side while R2 is reflectance from the uncoated side of glass
 10 and T is the Luminant transmission.

The H samples for Table 4 were exposed to 1200 degree F for approximately four minutes and then cooled to room temperature. The optical constants for sample 8 before heat treating are shown in table 5 below. These optical constant
5 are those used in other examples below.

TABLE 5

WAVELENGTH	REFRACTIVE INDEX	IMAGINARY REFRACTIVE INDEX
350.0	1.89450	0.09050
360.0	1.88140	0.07227
370.0	1.86920	0.05884
380.0	1.85800	0.04934
390.0	1.84750	0.04301
400.0	1.83770	0.03929
410.0	1.82850	0.03770
420.0	1.81990	0.03783
430.0	1.81180	0.03938
440.0	1.80420	0.04209
450.0	1.79700	0.04573
460.0	1.79020	0.05013
470.0	1.78370	0.05514
480.0	1.77760	0.06065
490.0	1.77170	0.06655
500.0	1.76610	0.07276
510.0	1.76070	0.07922
520.0	1.75550	0.08586
530.0	1.75060	0.09265
540.0	1.74580	0.09954
550.0	1.74120	0.10650
560.0	1.73670	0.11351
570.0	1.73240	0.12054
580.0	1.72820	0.12759
590.0	1.72420	0.13463
600.0	1.72020	0.14165
610.0	1.71630	0.14865
620.0	1.71250	0.15563
630.0	1.70880	0.16256
640.0	1.70520	0.16947
650.0	1.70160	0.17633
660.0	1.69810	0.18315
670.0	1.69470	0.18993
680.0	1.69120	0.19667
690.0	1.68790	0.20337
700.0	1.68460	0.21003
710.0	1.68130	0.21665
720.0	1.67800	0.22323
730.0	1.67480	0.22979
740.0	1.67150	0.23631
750.0	1.66830	0.24280
760.0	1.66520	0.24926
770.0	1.66200	0.25570
780.0	1.65880	0.26212
790.0	1.65570	0.26852
800.0	1.65260	0.27491

WAVELENGTH	REFRACTIVE INDEX	IMAGINARY REFRACTIVE INDEX
810.0	1.64940	0.28128
820.0	1.64630	0.28764
830.0	1.64310	0.29399
840.0	1.64000	0.30033
850.0	1.63680	0.30668
860.0	1.63370	0.31302
870.0	1.63050	0.31936
880.0	1.62730	0.32571
890.0	1.62410	0.33206
900.0	1.62090	0.33842
910.0	1.61770	0.34480
920.0	1.61450	0.35118
930.0	1.61120	0.35759
940.0	1.60790	0.36401
950.0	1.60460	0.37045
960.0	1.60130	0.37691
970.0	1.59800	0.38339
980.0	1.59460	0.38990
990.0	1.59120	0.39644
1000.0	1.58780	0.40301
1010.0	1.58440	0.40961
1020.0	1.58090	0.41624
1030.0	1.57740	0.42290
1040.0	1.57390	0.42960
1050.0	1.57040	0.43634
1060.0	1.56680	0.44311
1070.0	1.56320	0.44993
1080.0	1.55950	0.45679
1090.0	1.55580	0.46369
1100.0	1.55210	0.47064
1110.0	1.54840	0.47763
1120.0	1.54460	0.48467
1130.0	1.54080	0.49175
1140.0	1.53700	0.49889
1150.0	1.53310	0.50608
1160.0	1.52920	0.51332
1170.0	1.52520	0.52061
1180.0	1.52120	0.52796
1190.0	1.51720	0.53536
1200.0	1.51310	0.54282
1210.0	1.50900	0.55033
1220.0	1.50480	0.55791
1230.0	1.50070	0.56554
1240.0	1.49640	0.57324
1250.0	1.49220	0.58099
1260.0	1.48790	0.58881
1270.0	1.48350	0.59669
1280.0	1.47910	0.60463
1290.0	1.47470	0.61264
1300.0	1.47020	0.62072
1310.0	1.46570	0.62886
1320.0	1.46110	0.63707
1330.0	1.45650	0.64534
1340.0	1.45180	0.65369
1350.0	1.44710	0.66210
1360.0	1.44240	0.67058
1370.0	1.43760	0.67914
1380.0	1.43280	0.68777
1390.0	1.42790	0.69647

WAVELENGTH	REFRACTIVE INDEX	IMAGINARY REFRACTIVE INDEX
1400.0	1.42300	0.70524
1410.0	1.41800	0.71408
1420.0	1.41300	0.72300
1430.0	1.40790	0.73200
1440.0	1.40280	0.74107
1450.0	1.39760	0.75022
1460.0	1.39240	0.75944
1470.0	1.38720	0.76874
1480.0	1.38190	0.77812
1490.0	1.37650	0.78758
1500.0	1.37110	0.79712
1510.0	1.36560	0.80674
1520.0	1.36010	0.81643
1530.0	1.35460	0.82621
1540.0	1.34900	0.83607
1550.0	1.34330	0.84601
1560.0	1.33760	0.85604
1570.0	1.33190	0.86614
1580.0	1.32610	0.87633
1590.0	1.32020	0.88661
1600.0	1.31430	0.89697
1610.0	1.30830	0.90741
1620.0	1.30230	0.91794
1630.0	1.29630	0.92855
1640.0	1.29020	0.93926
1650.0	1.28400	0.95004
1660.0	1.27780	0.96092
1670.0	1.27150	0.97188
1680.0	1.26520	0.98293
1690.0	1.25880	0.99407
1700.0	1.25230	1.00530
1710.0	1.24580	1.01660
1720.0	1.23930	1.02800
1730.0	1.23270	1.03950
1740.0	1.22600	1.05110
1750.0	1.21930	1.06280
1760.0	1.21260	1.07460
1770.0	1.20580	1.08640
1780.0	1.19890	1.09840
1790.0	1.19190	1.11040
1800.0	1.18500	1.12260
1810.0	1.17790	1.13480
1820.0	1.17080	1.14720
1830.0	1.16370	1.15960
1840.0	1.15650	1.17210
1850.0	1.14920	1.18470
1860.0	1.14190	1.19740
1870.0	1.13450	1.21020
1880.0	1.12700	1.22310
1890.0	1.11950	1.23610

The NIR reflectors shown above are to help control the solar light transmittance through a window. The amount of solar light rejection is a function of many layers with a large total thickness. Many layers are needed to further

reduce the transmission of light through the glass. The application of a coating that selectively or preferentially absorbs NIR solar light as opposed to visible light would be helpful in making a good solar control stack. A single layer of antimony doped tin oxide, with the optical properties listed above, that is 800 angstroms thick will have about a 69% visible transmission and a 58% TSET. The transmission curve is compared to curve A from Figure 7 above and is shown in Figure 15. The coating does not have as high a transmittance in the visible but the TSET is comparable. When the visible light to TSET ratio is not needed to be high, or when the transmission of light through the window is needed to be low, such as for glare reduction, then the addition of an antimony layer to the stack is a good one. The antimony doped tin oxide layer can be combined with a fluorine doped tin oxide or other TCO to get both low emissivity and transmission reduction. Figure 16 shows the theoretical light transmission from a graded layer, antimony-doped tin oxide and fluorine-doped tin oxide coating. The TSET drops to 51% and the visible light transmission stays at about 69%. The TSET and visible light transmission can be altered with this design by varying the thickness of the antimony-doped tin oxide layer or by changing the antimony concentration in the coating.

Government regulations are driving the performance of windows. A new performance target for the southern USA is for windows to have a shading coefficient about 0.45. This can be achieved with a TSET of about 37%. The coating described for Figure 16 can be altered to reach this target by increasing the thickness of the antimony-doped tin oxide layer. The transmission curve for this coating is shown as curve A in Figure 17.

This coating has a visible light transmission of about 52% and a TSET of about 37%. The fluorine-doped tin oxide coating as the top layer will give this coating an emissivity less than about 0.35. The graded layer thickness is 800 angstroms, the antimony-doped tin oxide is 1800 angstroms and the fluorine-doped tin oxide is 1800 angstroms.

The TSET of this coating can be further reduced by the application of a quarter wave high index layer such as TiO_2 onto the top of the graded, antimony-doped tin oxide, fluorine-doped tin oxide discussed above. The TSET drops to 32.5% but the visible transmission only drops to 51%. The transmission curve of these stacks, with and without the TiO_2 layer, are shown in Figure 17 as curves B and A respectively below.

If low emissivity is not a requirement for the coating the fluorine-doped tin oxide, or other suitable transparent conducting oxide, can be removed leaving the graded layer, antimony-doped tin oxide and TiO_2 . The transmission curve for this coating is compared to the coating with fluorine-doped tin oxide in Figure 18.

A antimony-doped tin oxide coating, 2100 angstroms thick, on clear glass will have a visible transmission of 49% and a TSET of about 37%. The antimony-doped tin oxide thickness can be decreased to 1800 angstroms with the addition of a TiO_2 layer that is a quarter wave optical thickness at 1000nm. The TSET remains the same but the visible light transmission increased to 54%. The two curves are shown in Figure 19. The bold curve is the antimony-doped tin oxide with the TiO_2 layer.

The position of the TiO_2 or high index layer, relative to a graded color suppression layer and antimony-doped tin oxide and fluorine-doped tin oxide layer was studied. The graded index layer was first on the glass in all cases. The stack configuration is abbreviated as follows: S-substrate, G-graded index color suppression layer 800 angstroms thick, Sn-fluorine doped tin oxide 1600 angstroms thick, Ti - TiO_2 layer 1100 angstroms thick and Sb-antimony-doped tin oxide layer 1800 angstroms thick. The results are shown in Table 6. The addition of the TiO_2 or high index layer improves the TSET in all cases.

TABLE 6

EXAMPLE #	STACK	VISIBLE TR.	TSET
1	SGSbSnTi	50.6	32.4
2	SGSbTiSn	50.9	35.9
3	SGTiSbSn	52.2	35.1
4	SGTiSnSb	51.8	35.3
5	SGSnTiSb	51.5	36.0
6	SGSnSbTi	50.3	32.4
7	SGSnSb	51.4	36.8
8	SGSbSn	51.8	36.9

Two different five layer coatings were modeled to show the need for an absorbing layer in attaining a low TSET with a minimum of coating thickness. Curve A is a five layer coating of the configuration SHLHLH with TiO₂ as the high index layer and silica as the low index layer. Curve B is the same configuration but with F:SnO₂ as the low index layer. The design that contains SiO₂ is a total of around 6747 preferably 6747 angstroms thick, has a TSET of around but preferably 60% and a visible light transmission of around but preferably 85%. The design with fluorine-doped tin oxide has a total thickness of around but preferably 6461 angstroms, has a TSET of around but preferably 50% and a visible light transmission of around but preferably 71.1 percent. Clearly, the addition of additional layers will reduce the NIR transmission but this approach becomes cost prohibitive to produce because of the many thick layers. Even adding an additional pair of fluorine-doped tin oxide and TiO₂ layers, an additional 2700 angstroms in coating thickness, will only decrease the TSET by 5% and at the cost of 3.5 % visible transmission. It is very clear that the novel antimony-doped tin oxide described herein is preferred to achieve the desired TSET with minimum coating thickness.

A. Colorant

Two specific examples will be examined in detail. The first case is a coating to mask the green color of Solex® glass or Solargreen® glass and turn the glass gray. In this a thin layer of an antimony-doped tin oxide containing coating is

applied to the glass or coated glass. As the thickness of the coating is increased the transmitted color will shift from green to gray and if the coating is increased enough the transmitted color will shift to magenta. Based on the heat
5 treated coatings, the transmitted and reflected color will shift to a degree.

SOLAR CONTROL AND ANTI-REFLECTION FOR WINDSHIELD

As the installation angle of windshields increases the
10 reflectivity increases. Anti-reflection (AR) coatings will reduce the reflectance from 18% for Solargreen® glass to about 12-13% at an installation angle of about 65°. These traditional AR coatings do not impart any additional solar control properties but the increases in visible transmission
15 due to the AR properties can be used to darken the substrate and lower the TSET. An alternate approach to AR can be used to further reduce the TSET while imparting comparable AR performance to the traditional designs. This alternate approach does not require the modifications of the substrate
20 composition to attain the lower TSET. The UV/NIR coating with a top quarter wave of silica described above is used as the basis for this application (SHLHL/2 tuned for NIR). As the installation angle is increased the optical thickness of the coating decreases. The physical thickness of the layers can
25 be increased to compensate for this effect. The reflectance is reduced to 13% and the TSET is calculated to be about 37%.

The application of these solar control coatings provide a unique opportunity to further reduce the TSET of a windshield. If an AR coating is not necessary, the solar reflection can be
30 placed between the lites of the windshield. Conceivably two coatings, one on each lite, tuned to reflect different wavelengths, could reduce the TSET below 37% all while maintaining the target visible light transmission. The AR coating could also be applied to the inner lite of the Sungate®
35 windshield as disclosed in U.S. Patent. The NIR reflector properties of this coating could further improve the

properties of this product while imparting anti-reflection properties as well.

SELF CLEAN PROPERTIES

- 5 When titania is deposited in the anatase phase and exposed to UV light it becomes self-cleaning. Titania can be used as the high index layers in such designs. This will impart self-cleaning properties to the designs as well as the advanced solar control properties. These self cleaning
10 coatings can be applied as disclosed in Patent Cooperation Treaty (PCT) publication WO98/41480 published on September 24, 1998 and hereby incorporated by reference.

NIR WITH COLORED COATINGS

- 15 Transition metal oxides can be used to alter the reflected and transmitted color of glass for automotive use. The coatings provide a broad palette of colors, but the TSET of the coated glass can be improved. This is accomplished by combining transition metal oxides with the designs described
20 above to attain both solar control with the broad palette of colors.

- The transition metal oxides have a high refractive index can be used as the high index layer in these designs. If the color is too intense using exclusively the transition metal
25 oxides, then the transition metal oxides can be used as only one high index layer, or even as part of a high index layer. Alternately, the colored transition metal oxide can be combined with a non-colored oxide to mute the color of the coating. Using either of these techniques, one can attain
30 both solar control with a variety of colors. One could even have different colored materials for the various high index layers, giving the designer even more choices for controlling the color of the coated glass.

I CLAIM:

1. A multilayered coated article, comprising:
 - a) transparent substrate selected from the group of clear
5 glass, tinted glass, solar control glass, and colored glass;
 - b) first metal-containing predominantly inorganic coating layer that has visual transparency and has a refractive index selected from the group of high and low;
 - c) a second metal-containing predominantly inorganic
10 coating layer that has visual transparency and has a refractive index opposite from the refractive index of the first coating; and
 - d) a third metal-containing predominantly inorganic coating layer that has visual transparency and has a
15 refractive index in the range of that of the first coating layer.
2. Article of Claim 1 wherein the coating layer with
20 the high refractive index has the refractive index higher than the low refractive index of the other coating layer and the coating layer with the low refractive index has the refractive index lower than the high refractive index of the coating layer with the high refractive index.
- 25 3. Article of Claim 1 wherein the coating layer with the high refractive has a refractive index that is greater than around 1.75 and the coating layer with the low refractive index has a refractive index that is less than around 1.75.
- 30 4. Article of Claim 1 wherein the coating layer with the high refractive has a refractive index that is greater than 1.9 and coating layer with the low refractive index has a refractive index that is less than 1.6.
- 35 5. The article of claim 1, wherein the first coating layer is selected from titania and silica and the second coating layer is silica when titania is the first coating

layer and titania when the first coating layer is silica and the third coating layer is the same as the first coating layer.

5 6. Article of Claim 5 which has a transparent conducting oxide coating as part of the middle third of the inner silica coating layer to have a middle layer comprised of a combination of several coating layers so that the transparent conducting oxide provides for a high refractive
10 index in the UV and visible spectrum but a low refractive index in the NIR to give a five layer coating coating stack configuration of S3HLHL3H in the UV and a three layer coating stack with the configuration of SHLH in the NIR. The coating is effectively a five layer coating in the UV and visible but
15 reduces to a three layer coating in the NIR to result in increasing the intensity of the UV reflectance without increasing the total thickness of the coating stack and sacrificing the intensity of the NIR reflectance.

20 7. Multilayered coated article of claim 1 wherein the coating layers absorb more NIR than visible light.

 8. Multilayered coated article of claim 1 wherein the coating layers absorb equally in the NIR and visible light
25 portions of the light spectrum.

 9. Multilayered coated article of claim 1 wherein the coating layers absorb more visible light than NIR.

30 10. Multilayered coated article of claim 1 wherein at least one of the coating layers has antimony doped tin oxide with a concentration of dopant and a thickness of the coating layer to absorb light around 500 nanometers thereby changing the transmitted color of a green substrate.

35

 11. Article of Claim 1 wherein the coating layer with the high refractive index is from a material having a high

refractive index in the UV and visible part of the light spectrum and a low refractive index in the NIR part of the spectrum.

5 12. Article of Claim 1 wherein the refractive index is from fluorine-doped tin oxide.

13. Article of Claim 1 which has a fourth coating layer that absorbs light across the entire solar spectrum for
10 control of the relative absorption at different wavelengths by altering the deposition process to tune the coating to absorb relatively more light selected from the group consisting of visible light, UV light, and NIR light.

15 14. Article of Claim 13 wherein the fourth coating layer is antimony-doped tin oxide.

15. Article of Claim 1 which has an optically invisible at least one $\frac{1}{2}$ wave coating layer on top of the SHLH stack so
20 that the stack SHLHLL behaves the same as the stack SHLH and there is no alteration of the UV rejection performance.

16. Article of Claim 15 where for a design wavelength in the UV, the top half wave of silica LL, is a quarterwave in
25 the visible spectrum which acts as a visible spectrum reflectance reducing layer by having a layer thickness for UV blocking and visible light transmission.

17. Article of Claim 1 wherein the design wavelength is
30 330 nm. which minimizes ISO UV while for a green glass at a thickness of 3.6 mm glass maintains a visible light transmission above 70%.

18. Article of Claim 1, which has interlayered into the
35 initial SHLH stack designed for 350nm halfwave coating layers for each layer to get the S3H3L3H stack so that the coating layer stack behaves identically at the 350nm design

wavelength, but is an SHLH stack at near 1050nm which is around the reflectance maximum so that the refractive index of the coating layer is less at the longer wavelengths and the peak is shifted to shorter wavelengths in the NIR part of the spectrum so that the coating stack reflects at two design wavelengths.

19. Article of Claim 1 which has a coating layer that is a 1/4 wave in the visible spectrum and a 1/8 wave in the NIR at 1050nm and a 1.5 wave in the UV at 350 nm. to alter the intensity of the reflection in the visible spectrum.

20. Article of Claim 1 which has a transparent conducting oxide coating layer on at least one side of the HLH coating layer stack.

21. Article of Claim 20 wherein the transparent conducting oxide is fluorine-doped tin oxide and the coating layer of high refractive index is of titanium dioxide.

22. Article of Claim 20 which includes at least one LH refractive index coating layer pair to increase the reflectance peak.

23. Article of Claim 1 which includes a coating layer to dampen the reflected color by the coating layer having an intermediate refractive index between the substrate and the first coating layer of high refractive index.

24. Article of Claim 1 which includes a coating layer to dampen the reflected color by the coating layer having an intermediate refractive index over the last high index coating layer.

25. Article of Claim 1 which includes a graded coating layer of varying refractive index through the thickness of the

coating layer along with at least one HLH stack of coating layers.

26. Article of Claim 1 which are tempered.

5

27. Article of Claim 1 having a dual NIR and UV rejection coating layer stack with silica and transparent conductive oxide coating layers acting as the low refractive index layer.

10

28. Article of Claim 27 wherein the stack of coating layers on the glass substrate has titanium oxide, at least one pair of coating layers of silica and transparent conductive oxide, and titanium dioxide, wherein the silica and transparent conductive oxide coating pair has a combined optical thickness in the NIR of a quarter wavelength.

15

29. Article of Claim 27 wherein the transparent conductive oxide is fluorine doped tin oxide.

20

30. Article of Claim 27 wherein the coating layer stack has a graded refractive index layer, antimony doped tin oxide and fluorine doped tin oxide.

25

31. Article of Claim 1 having a five layer coating stack selected from the group of: a coating stack with the configuration SHLHLH with TiO₂ as the high index layer and silica as the low index layer with a total thickness of around 6747 angstroms, a TSET of around 60% and a visible light transmission of around 85%; and with the same configuration where F:SnO₂ is the low index layer with a total thickness of around 6461 angstroms, a TSET of around 50% and a visible light transmission of around 71.1%.

30

32. Article of Claim 1 wherein the glass substrate has green color and has a thin layer of an antimony-doped tin

35

oxide containing coating at a thickness of the coating layer to shift the transmitted color from green to magenta.

33. Article of Claim 1 wherein the coating layer with
5 the high refractive index includes the transition metal oxides having a high refractive index used as the high index layer where color intensity is reduced by the transition metal oxides used as only one high index layer in the coating stack, or as part of a high index layer and the colored transition
10 metal oxide can be combined with a non-colored oxide to mute the color of the coating to attain both solar control with a variety of colors.

34. A multilayered coated windshield having an
15 ultraviolet transmission of less than 10 percent and a total solar energy transmission of less than 50 percent, while also having a visible light transmission of greater than 70 percent, comprising:

- a) transparent substrate selected from the group of
20 tinted glass, solar control glass, and colored glass;
- b) first metal- containing coating layer having with a refractive index selected from the group of high and low;
- c) a second metal-containing coating layer having a refractive index different as opposite from the first
25 refractive index,
- d) a third metal-containing predominantly inorganic coating layer having a refractive index in the range of that of the first coating layer.

30 35. Article of Claim 34 wherein the UV/NIR coating with a top quarter wave of silica has a configuration of SHLHL/2 tuned for NIR as the installation angle of the windshield in the opening of the motor vehicle is increased the optical thickness of the coating decreases and the physical thickness
35 of the layers are increased to compensate so that to further reduce the TSET of a windshield.

36. Article of Claim 34 wherein the coating layers for solar reflection are placed on different substrate surfaces to be between the substrates as lites of the windshield without an antireflective coating layer.

5

37. Article of Claim 1 wherein the substrate is essentially free of CeO_2 .

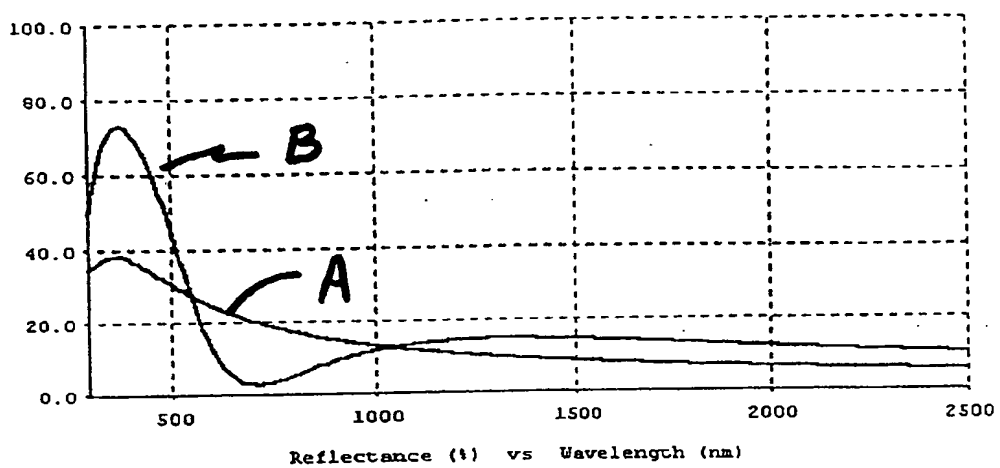


FIGURE 1

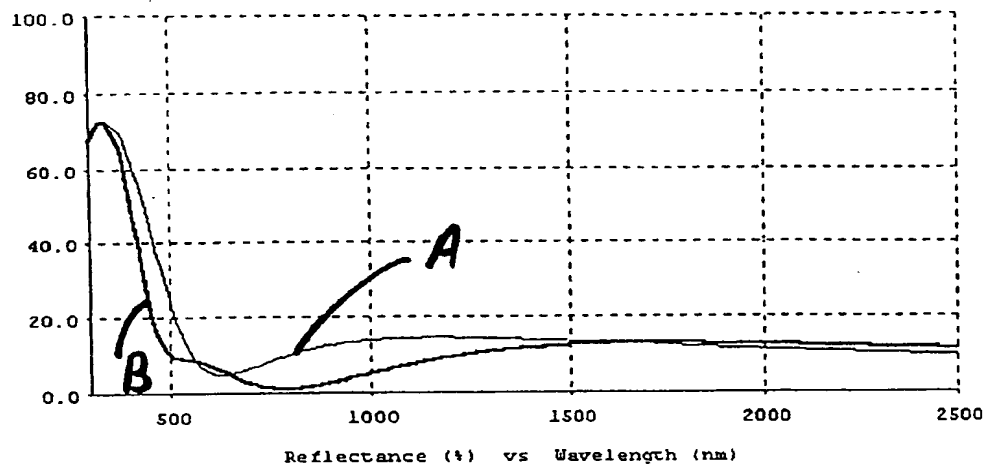


FIGURE 2

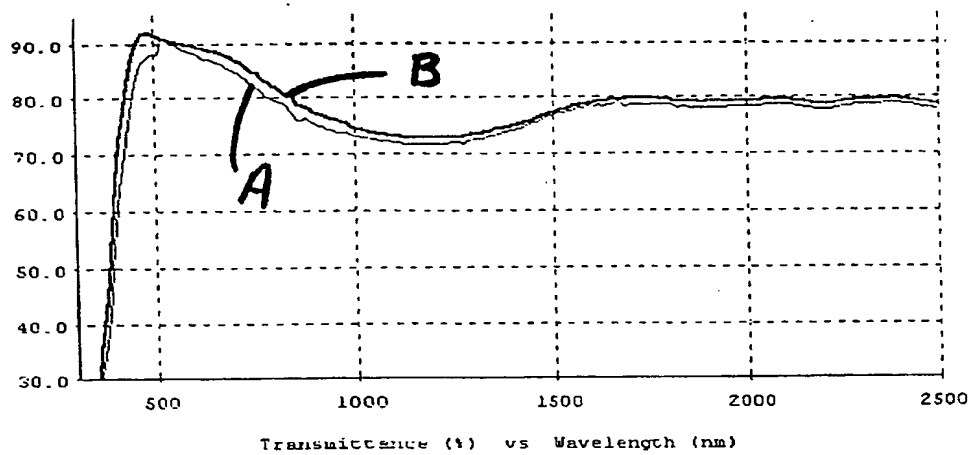


Figure 3

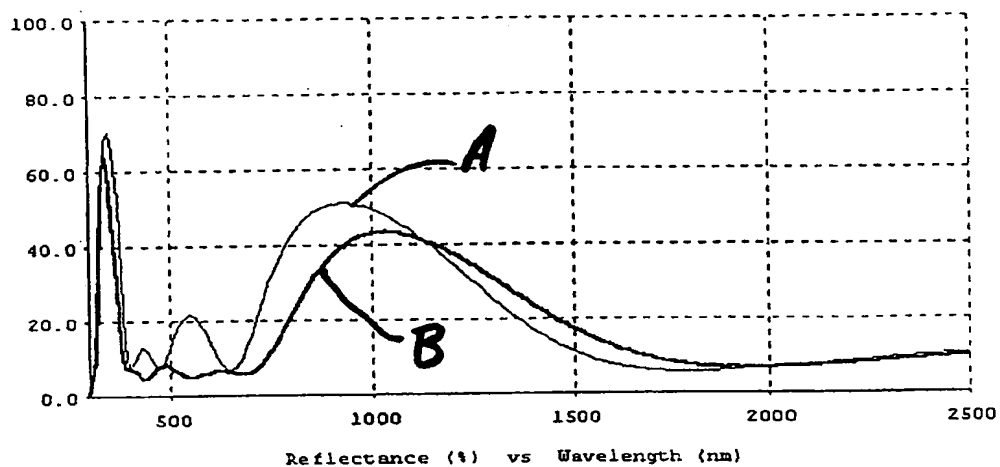


FIGURE 4

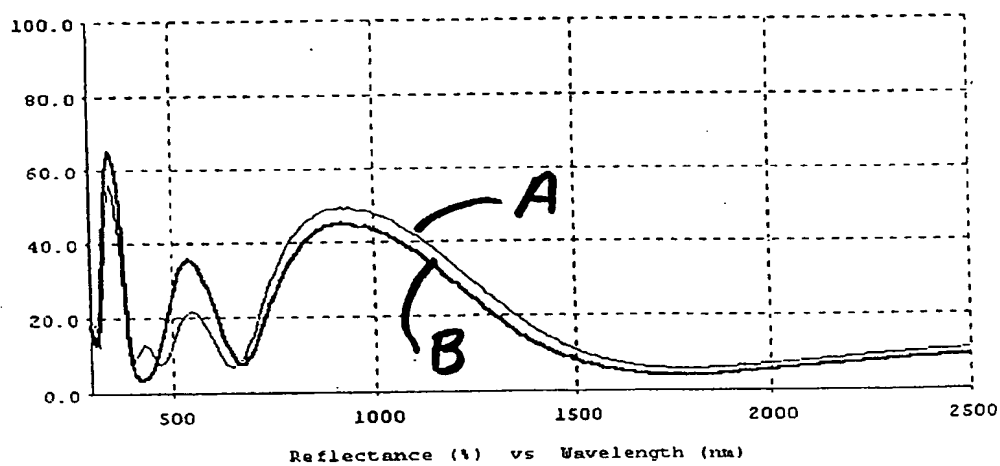


FIGURE 5

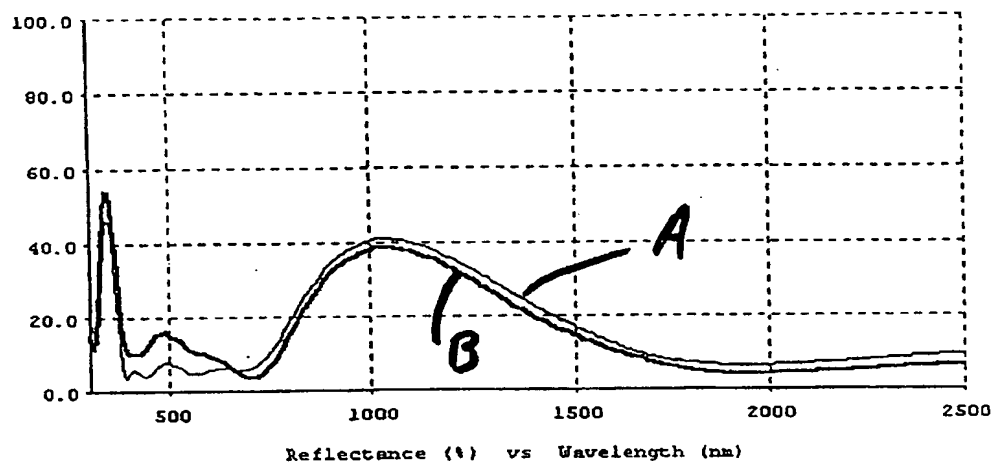


FIGURE 6

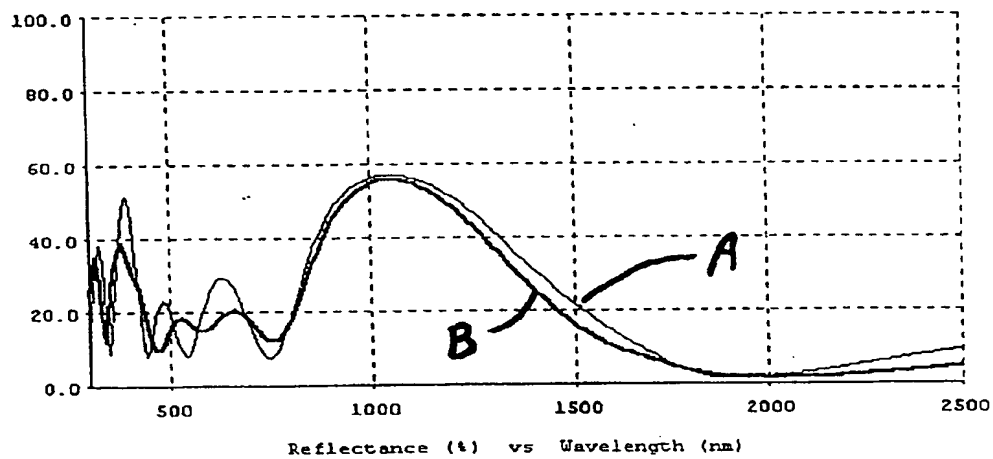


FIGURE 7

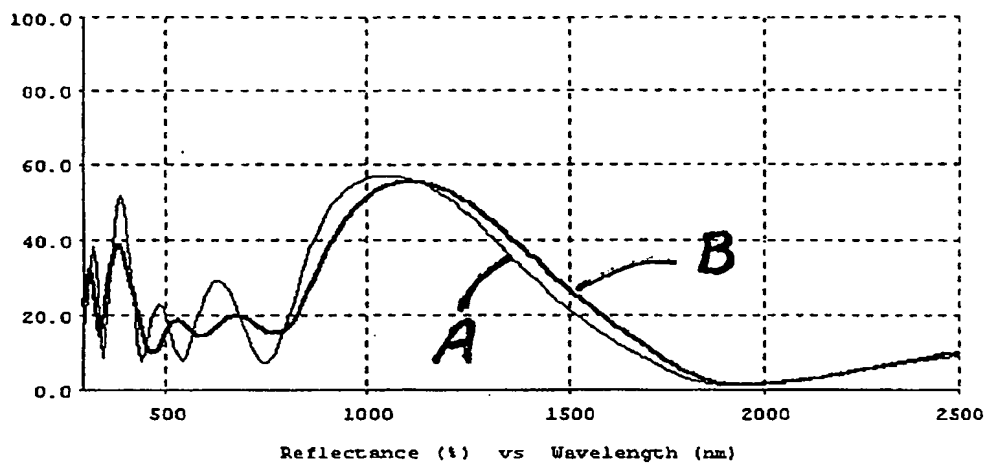


FIGURE 8

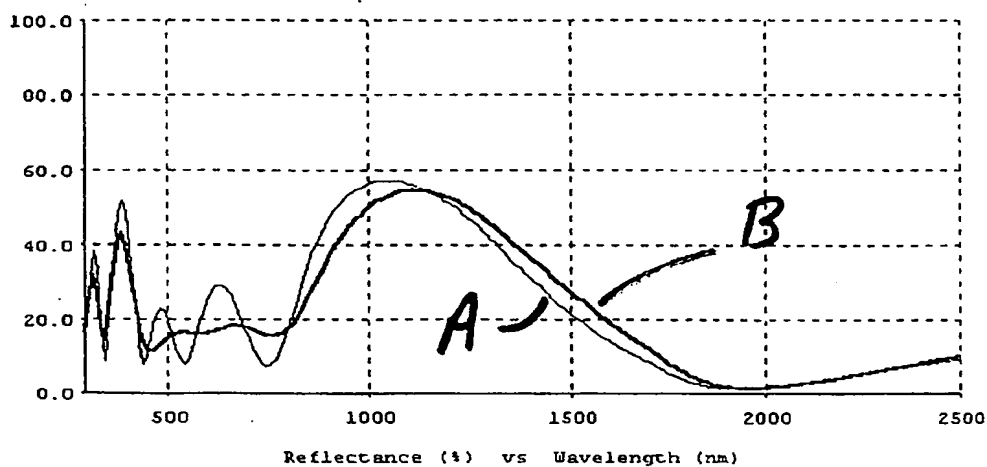


FIGURE 9

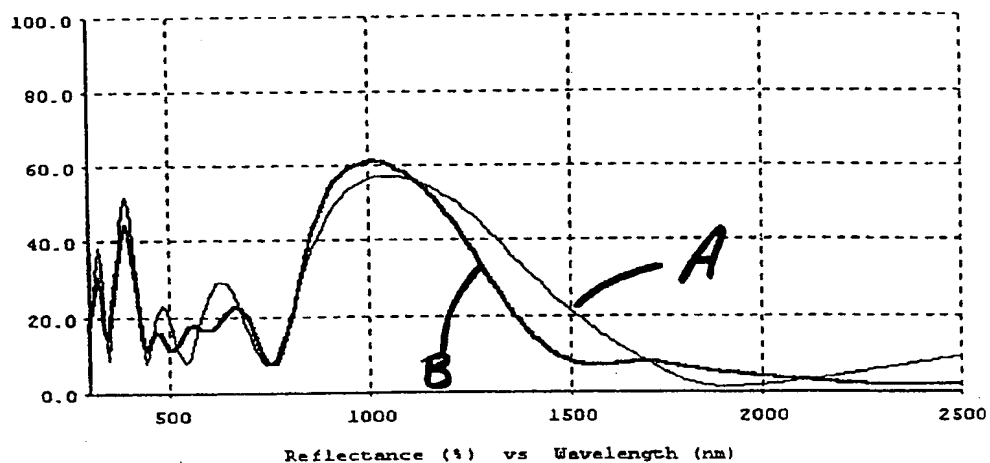


FIGURE 10

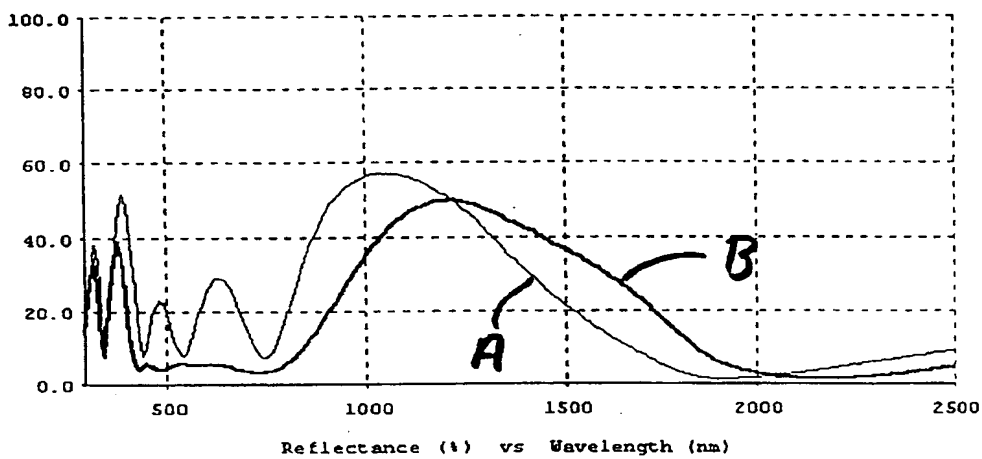


FIGURE 11

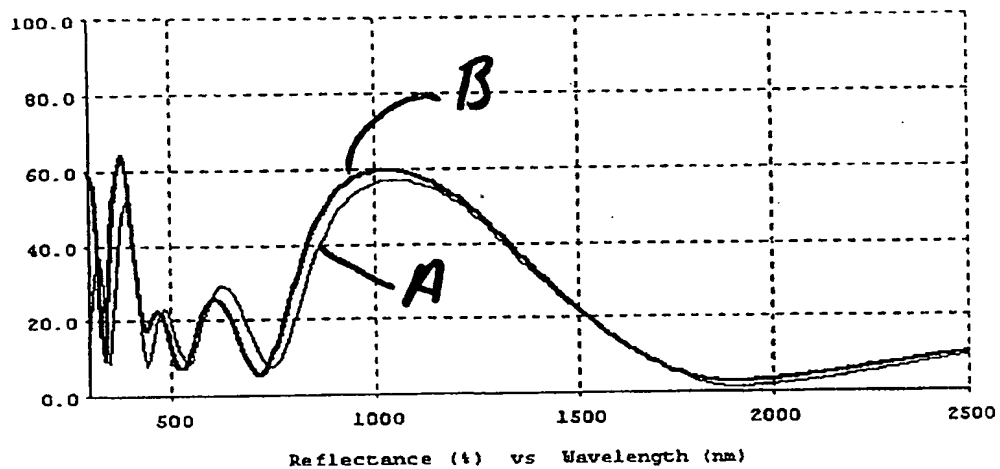


FIGURE 12

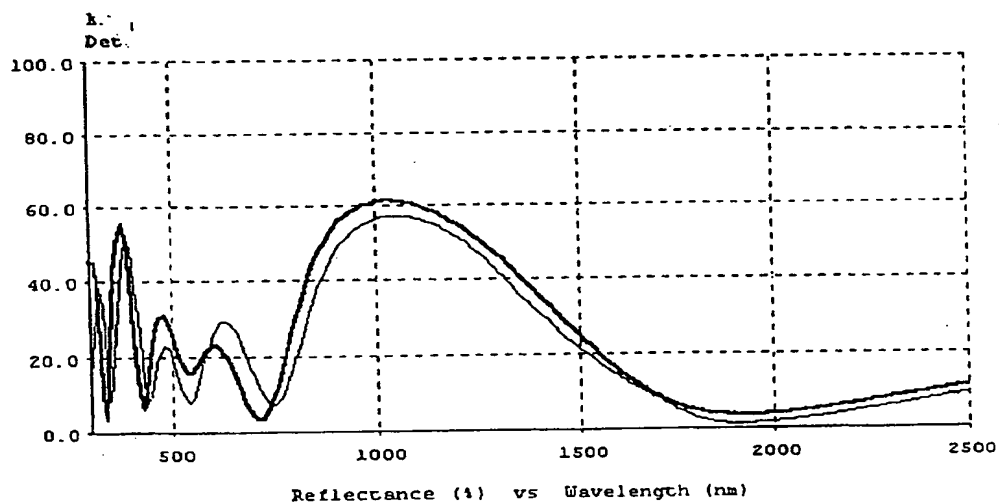
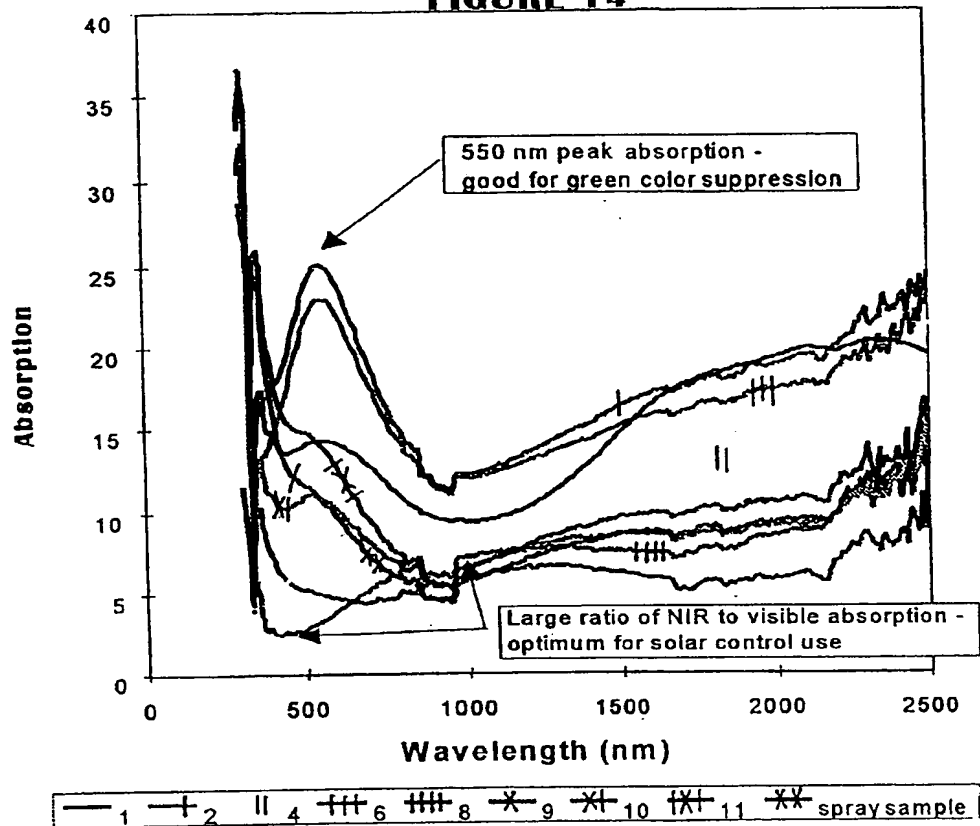


FIGURE 13

Antimony⁸/Doped¹¹ Tin Oxide Absorption Study

FIGURE 14

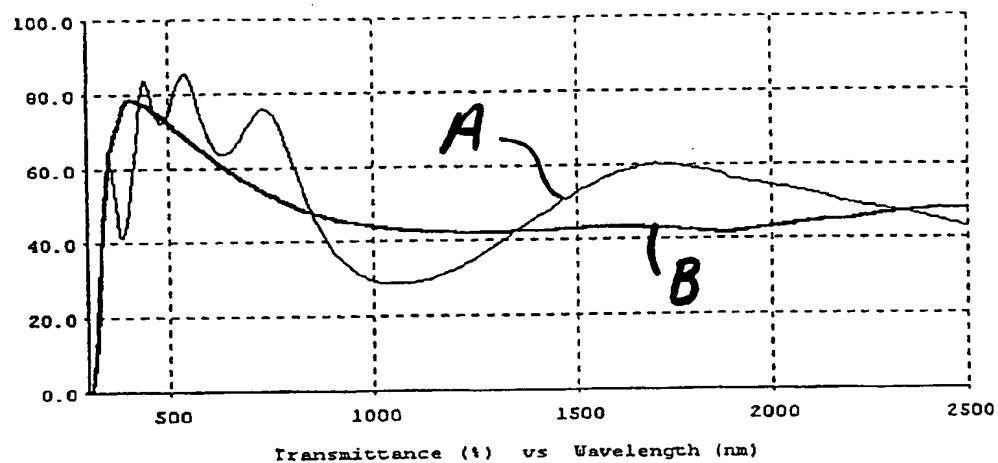


FIGURE 15

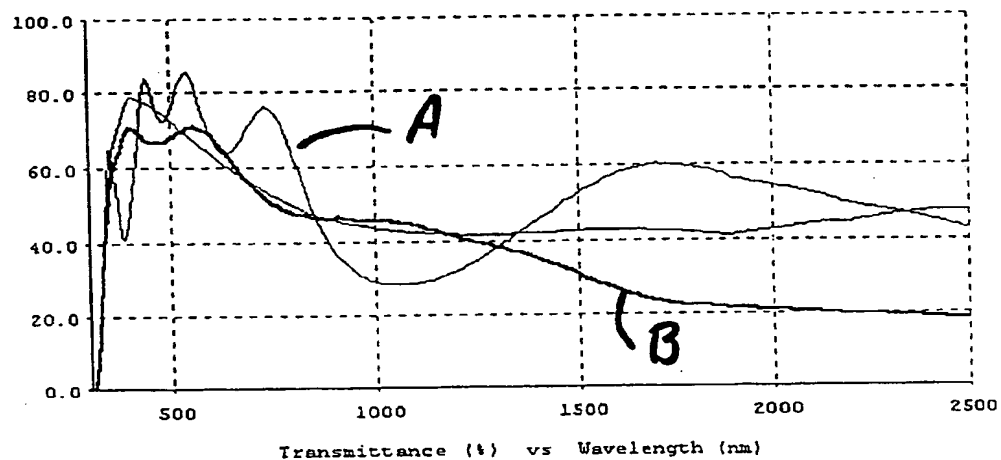


FIGURE 16

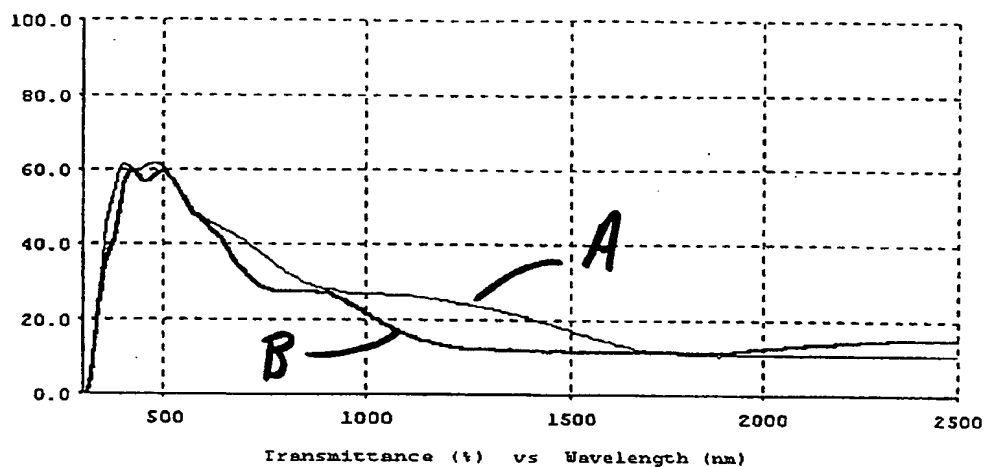


FIGURE 17

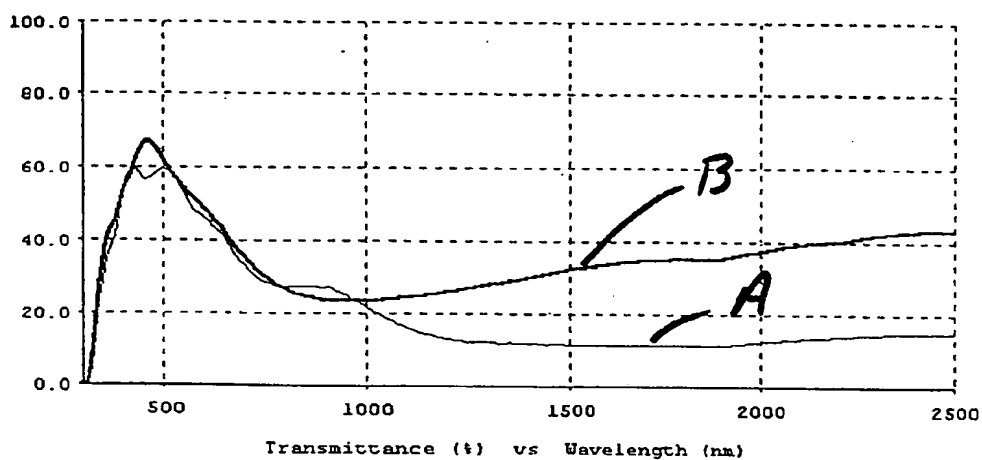


FIGURE 18

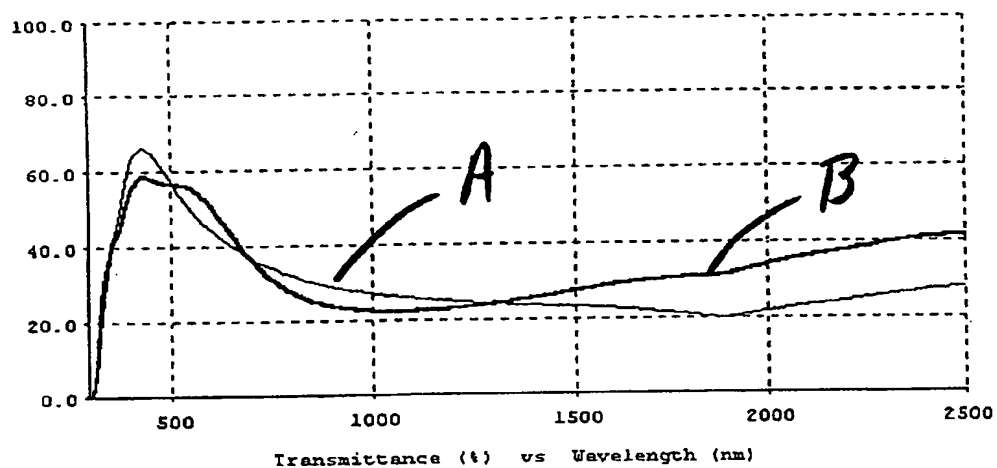


FIGURE 19

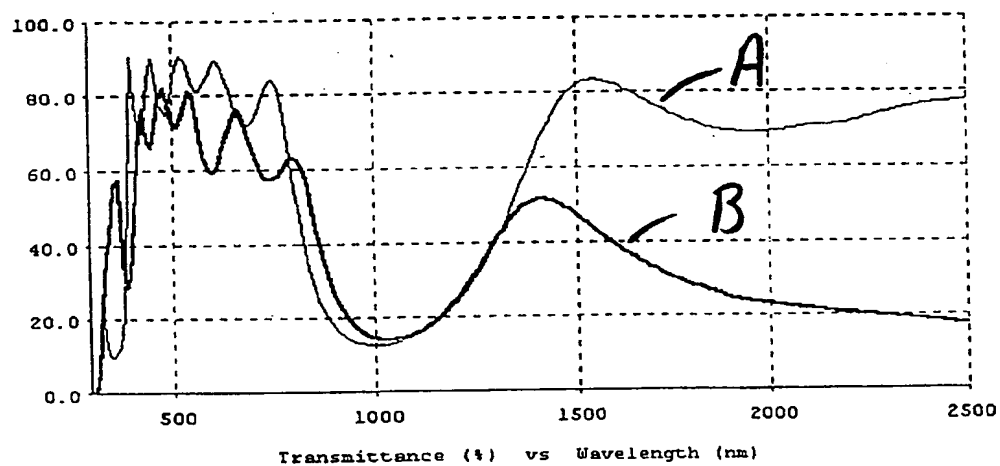


FIGURE 20

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 99/26406

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C17/34 G02B5/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 25201 A (LIBBEY OWENS FORD CO) 17 July 1997 (1997-07-17) claims	1-5, 7-14, 18, 20, 21, 26, 32, 34, 36, 37
X	US 5 667 880 A (OKANIWA MASAYUKI) 16 September 1997 (1997-09-16) claims; examples	1-5, 7-14, 18, 20, 21, 26, 32, 34, 36

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "O" document referring to an oral disclosure, use, exhibition or other means
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

9 March 2000

Date of mailing of the international search report

16/03/2000

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Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 99/26406

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GB 2 324 098 A (PILKINGTON PLC ; LIBBEY OWENS FORD CO (US)) 14 October 1998 (1998-10-14) claims	1-5, 7-14, 18, 20, 21, 26, 32, 34, 36
X	DE 40 24 338 A (SIEMENS AG) 21 February 1991 (1991-02-21) claims; examples	1-5, 7-9, 13, 15, 18, 26, 31, 34-37
X	US 4 099 840 A (VAN DER WAL JOHANNES ET AL) 11 July 1978 (1978-07-11) claims; examples	1-5, 7-9, 13, 15, 18, 26, 31, 34-37
X	US 4 128 303 A (ONOKI FUMIO ET AL) 5 December 1978 (1978-12-05) claims	1-4, 7-9, 13, 15, 18, 26, 31, 34-37
X	WO 92 04185 A (VIRATEC THIN FILMS INC) 19 March 1992 (1992-03-19) claims	1-4, 7-9, 13, 15, 18, 26, 31, 34-37
X	GB 2 121 075 A (TOYODA CHUO KENKYUSHO KK) 14 December 1983 (1983-12-14) claims; examples	1-4, 7-9, 13, 15, 18, 26, 31, 34-37
X	US 5 170 291 A (SZCZYRBOWSKI JOACHIM ET AL) 8 December 1992 (1992-12-08) claims	1-4, 7-9, 13, 15, 18, 26, 31, 34-37
X	DE 41 00 820 A (JENOPTIK JENA GMBH) 8 August 1991 (1991-08-08) claims; examples	1-5, 7-9, 13, 15, 18, 26, 31, 34-37
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INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 99/26406

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 520 720 A (FORD MOTOR CO ; FORD FRANCE (FR); FORD WERKE AG (DE); FORD MOTOR CO) 30 December 1992 (1992-12-30) claims; examples	1-5,7-9, 13,15, 18,26, 31,34-37
X	EP 0 521 602 A (FORD MOTOR CO ; FORD FRANCE (FR); FORD WERKE AG (DE); FORD MOTOR CO) 7 January 1993 (1993-01-07) claims; examples	1-5,7-9, 13,15, 18,26, 31,34-37
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 535 (C-0781), 26 November 1990 (1990-11-26) & JP 02 225345 A (NIPPON SHEET GLASS CO LTD), 7 September 1990 (1990-09-07) abstract	1-5,7-9, 13,15, 18,26, 31,34-37
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 254 (C-308), 11 October 1985 (1985-10-11) & JP 60 108347 A (TOYOTA JIDOSHA KK), 13 June 1985 (1985-06-13) abstract	1-5,7-9, 18,26, 33,34, 36,37
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